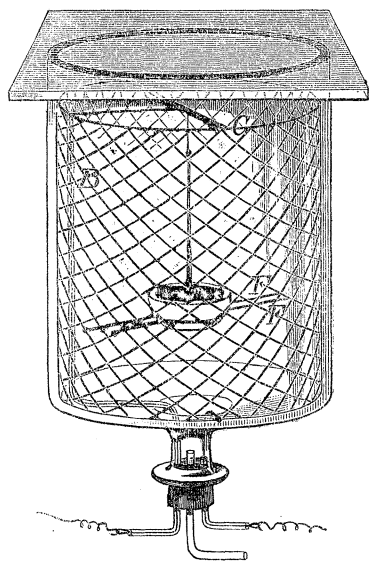


V. "On the Electrolysis of Silver Nitrate *in Vacuo*." By
ARTHUR SCHUSTER, F.R.S., and ARTHUR W. CROSSLEY,
B.Sc. Received January 5, 1892.

The following investigation was undertaken in order to clear up some minor irregularities which occur when the intensity of an electric current is measured by means of a silver voltameter.

The electrolysis of silver nitrate yields with moderate precautions such very consistent results that it seemed of interest to follow up the small apparent deviations from Faraday's laws which are found to exist. One of these irregularities has been noticed by Lord Rayleigh, who found that the deposit of silver from a hot solution was about one part in two thousand heavier than the deposit from a cold solution. A second anomaly lies in a small but regular discrepancy in the deposits when these are taken simultaneously in platinum bowls of different sizes; the difference, according to our experiments, seems to depend on the current density at the *anode*. But the chief part of this paper will deal with the fact discovered by us, that the deposits are slightly larger when the electrolysis is conducted *in vacuo* than when, as usual, the voltameters are exposed to air at the ordinary pressure. This difference we trace to the effects of dissolved

FIG. 1.



oxygen, for when the electrolysis is carried out in an atmosphere of oxygen the deposits are smaller than those obtained in air.

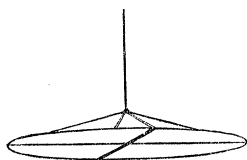
The apparatus we employed to obtain a deposit *in vacuo* is illustrated in fig. 1. An inverted bell-jar, closed at the bottom by an india-rubber stopper and at the top by a plate of glass, contains a tight-fitting cylindrical cage of wire gauze, which serves as support to the electrodes. The platinum basin is placed on two stout copper wires, F, which are soldered to the cage. Metallic contact between the wires and the bowl is secured by the help of tinfoil, which is wrapped round the wires and forms a cushion on which the bowl rests. One of the wires leading to the battery is soldered to the cage. The anode is suspended from a glass rod, C, fixed to the cage near its upper end, the current being conveyed to the anode by an insulated wire passing through a glass tube, B, which is also secured to the cage. Three pieces of glass tubing pass through the india-rubber stopper; one serves to exhaust the vessel, while the wires leading to the battery pass through the remaining two.

The stopper is rendered air-tight by means of Faraday cement, and some grease has to be used to prevent leakage between the glass plate and bell-jar. To prevent particles of this grease contaminating the solution, a tightly-fitting piece of cardboard, not shown in the figure, was placed above the cage. In the latter part of the investigation two nearly identical bell-jars were used.

The same current always passed through two or three voltmeters in succession, and the deposits obtained simultaneously were compared with each other. One of the platinum bowls, to be referred to as the large bowl, has a diameter of 5 inches, while the smaller bowl had a diameter of $3\frac{1}{2}$ inches.

The silver anodes had a thickness of about 2 mm., and generally larger anodes were used in the large bowl than in the small one. With respect to the contact between the anodes and the platinum wires conveying the current, it seems worth while to draw attention to a precaution, which, if neglected, may cause serious trouble. We placed at first, for the sake of convenience, the anodes simply into two loops of platinum wire. These loops crossed at right angles as in fig. 2. The current under these circumstances is apt to pass partly from the platinum wires, and dark red crystals (probably

FIG. 2.



Ag_2O_2) then shoot out rapidly and form a bridge across the electrolyte.

We have not observed similar effects when the silver plates were perforated, and the platinum wires which passed under the silver plate were everywhere in metallic contact with it. We used filter-paper to cover the anodes, and followed generally Lord Rayleigh's instructions regarding the conduct of the experiment. The platinum basins were in some experiments first cleaned out with sand, but often this was not done. They were then washed with (1) concentrated nitric acid, (2) strong caustic soda, (3) tap water, (4) distilled water. They were dried roughly with a clean silk handkerchief and heated over a Bunsen flame. After an hour's cooling they were weighed. The deposits of silver were washed three or four times with distilled water, and allowed to stand under water for a night; they were then again washed several times and dried in an air-bath at first at 100°C. ; the temperature was finally raised to 160° for ten minutes. After an hour's cooling, the final weighings were taken.

In a large number of experiments it almost certainly happens that some anomalous results are obtained, either through insufficient washing or through loss of small quantities of silver. We give, without exception, the result of each experiment, and think that on the whole they show a remarkable consistency in the indications of the silver voltmeters. The effects we investigate are the differences in the deposit of less than one part in a thousand, and the possibility of investigating these differences is a proof that the electrolysis of silver nitrate can safely be trusted to that degree of accuracy.

The only serious source of error against which we had to guard was the prevention of leakage in the leads between the two voltmeters.

That our results can in no way be attributed to such leakage is shown by the fact that the voltmeters were used in the same position with the bell-jar exhausted or full of air. When the jar was full of air, the difference in the deposit disappeared, except for the small anomaly due to the different sizes of the basins.

When the jar is exhausted, it might be thought that a film of moisture could condense outside the platinum bowl, owing to the cooling due to evaporation in an atmosphere saturated with vapour. If such a film were to a certain extent to short-circuit the bowl, a smaller deposit would be formed *in vacuo*; but our effect is an increase, not a diminution, of the deposit. Our leads were all carefully insulated, and as the resistance of the voltmeters was never more than 1 ohm, there is no difficulty in avoiding leakage to the extent required.

For the sake of clearness, we do not give our results in the order in which they were obtained, but the numbers attached to each

Table I.

Number of experiment.	Date.	Strength of solution in per cent.	Approximate current in ampères.	Duration of electrolysis in minutes.	Weight of deposits.		Difference in mgrms.	Percentage difference.
					Large bowl.	Small bowl.		
4	Jan. 15	12	0·58	34	1·3223	1·3220	+0·3	0·023
7	" 27	12	0·70	30	1·4229	1·4226	+0·3	0·021
9	Feb. 2	12	0·59	120	4·7616	4·7606	+1·0	0·021
15	March 25	15	0·56	60	2·2364	2·2361	+0·3	0·014
16	" 31	15	0·55	60	2·2068	2·2060	+0·8	0·036
12	March 17	12	0·78	60	3·1653	3·1686	-3·3	-0·106
13	" 19	15	0·83	60	3·3518	3·3517	+0·1	0·003
14	" 23	15	0·55	60	2·2410	2·2410	+0·0	0·000

experiment represent the order in which they were made. We begin by comparing together the deposits obtained in bowls of different sizes, both being in air.

With the exception of the last three observations, the results give a consistent difference of about two parts in ten thousand in favour of the larger bowl. With respect to the last three observations, we have to offer the following explanation :—In order to trace, if possible, the difference between the results obtained with large and small bowls, we used in these experiments two anodes of the same size, while in all other cases the anodes were approximately proportional to the size of the bowl. Experiment 12 is anomalous ; we cannot account for the difference of 3 milligrams in favour of the small bowl, and simply record the observation ; but do not think that this one experiment can render the results of the others doubtful, especially when taken in conjunction with Lord Rayleigh's observations, presently to be referred to. Experiments 13 and 14 seem to show that when anodes of the same size are used the discrepancy between the bowls disappears. This confirms an impression we have gained that the effect is possibly due to secondary products formed at the anode when the current density there exceeds a certain value. It seems certain that too great a current density at the anode is accompanied by a smaller deposit, but our experiments are not sufficient to decide whether the systematic difference in the two bowls is to be ascribed to the same cause.

Table II.—Comparison of Deposits obtained by Lord Rayleigh in Large and Small Bowls.

Date.	Deposit in large bowls.	Deposit in small bowls.	Difference in mgrms.	Percentage difference.
	grms.	grms.		
Nov. 29	3·0166	3·0165	+0·1	+0·003
Dec. 4	2·9907	2·9902	+0·5	+0·017
Feb. 18	2·3484	2·3482	+0·2	+0·009
		2·3483	+0·1	+0·004
Feb. 22	3·2977	3·2966	+1·1	+0·033
		3·2979	−0·2	−0·006
Feb. 29	2·2698	2·2693	+0·5	+0·022
		2·2701	−0·3	−0·013
Mar. 5	1·2247	1·2247	±0·0	±0·000
		1·2248	−0·1	−0·001
Mar. 10	1·0648	1·0643	+0·5	+0·047
		1·0645	+0·3	+0·028
Mar 14	1·2897	1·2892	+0·5	+0·039
		1·2893	+0·4	+0·031
Mean.....				+0·015

Lord Rayleigh in his experiments on the silver voltameter used two bowls of approximately the same size as ours, and the foregoing comparison will show that the difference in the deposits pointed out by us also appears in his results.

In Table II we have entered in two separate columns the deposits obtained by Lord Rayleigh simultaneously from silver nitrate solutions in large and small bowls respectively.

The mean deposit in the large bowls is therefore greater by approximately the same amount as in our experiments. In three cases only were the deposits in the small bowls heavier; and in two out of these three cases the bowl showing these larger deposits contained a 30 per cent. solution, while the other at the same time was filled with a 15 per cent. solution. It seems possible, therefore, that when the strength of the solution is increased to 30 per cent. the difference due to the size of the bowls will disappear. We have recalculated Lord Rayleigh's value for the equivalent of silver, taking the deposits in the large and small bowls separately, using the weight of silver deposited before heating to verge of redness; we find for the equivalent of silver:

(a)	calculated from deposits in large bowls	0·0111817
(b)	" " small " 	0·0111797
Mean		0·0111807

The heating to redness seems to affect the deposits equally, and reduces the weight, on the average, by about one part in ten thousand, which accounts for the difference between the above mean and the equivalent as given by Lord Rayleigh and Mrs. Sidgwick.

In some of our later experiments we used three voltmeters in series, two of them being kept in an exhausted receiver.

This arrangement allowed us to judge whether the difference in the results obtained with large and small bowls persisted *in vacuo*. The results are not very concordant, but the average deposits are heavier in the large bowl, and hence we do not believe that the influence of current density can be ascribed to the presence of air in the solution.

In Experiment 27 the manipulation differed, in so far as the bowls were cleared out with sand before use: a proceeding adopted in the first experiments as far as the eleventh, but abandoned afterwards. We cannot, of course, draw any conclusions from a single experiment, but it does not seem impossible that the complete removal of the old surface by washing with sand renders the effect of current density more prominent. There is, no doubt, a difference in the condition under which the electrolysis is carried out, according as the deposit takes place on platinum as in the first few seconds, or on silver as in

Table III.—Pressure about $1\frac{1}{8}$ inches.

Number of experiment.	Date.	Strength of solution in per cent.	Approximate current in amperes.	Duration of electrolysis in minutes.	Weight of deposits.		Difference in mgrms.	Percentage difference.
					Large bowl.	Small bowl.		
18	April 30	20	0·5	60	1·9740	1·9736	+0·4	+0·022
19	May 4	20	0·5	60	2·0239	2·0231	+0·8	+0·040
20	"	20	0·5	60	2·0088	2·0090	-0·2	-0·010
21	"	12	0·5	60	2·0566	2·0562	+0·4	+0·020
22	"	12	0·45	60	1·8785	1·8781	+0·4	+0·021
23	"	12	0·75	40	2·0470	2·0469	+0·1	+0·005
24	"	12	0·75	40	2·0255	2·0252	+0·3	+0·015
25	"	12	0·5	30	1·0117	1·0120	-0·3	-0·030
26	"	12	0·5	30	0·9795	0·9796	-0·1	-0·010
27	"	12	0·5	30	1·0057	1·0039	+1·8	+0·180
Sum including 27					17·0112	17·0076	+3·6	+0·021
Sum excluding 27					16·0055	16·0037	+1·8	+0·011

the later stages, and after a number of experiments there may be a thin layer of silver, possibly an alloy of silver and platinum, which resists the action of acid, and can only be scraped out with sand. It is to be noted that Kohlrausch took his silver deposits on platinum which had previously been covered with a layer of silver; while in Lord Rayleigh's experiments the silver deposits were removed from the dish before a new experiment was made. The difference may account for the somewhat greater equivalent found by Kohlrausch; but the concordance of the results shows that there can be no systematic difference amounting to more than a few parts in ten thousand.

We turn now to the main part of the investigation, which is the comparison of the deposits obtained in air and *vacuo*. The solution used in the different voltameters was always taken out of the same bottle. We had intended in this way to make sure that any difference in the deposits was not due to some chemical difference in the solutions. It did not occur to us at the time that the solution in one voltameter being freed of air, we should gradually diminish the amount of air also in the other voltameter, for the solutions were kept in stoppered bottles, which did not allow of a ready re-absorption of oxygen. It will be seen that the differences in the deposits, when these were taken in air and *vacuo*, were larger and more regular in the first experiments than later on, and this may have been due to the gradual elimination of oxygen out of the solution.

Our first experiments were made with the large bowl placed *in vacuo*, and the small one in air. The results, to which a later one is added for the sake of completeness, are embodied in Table IV. Experiment 17 was not a satisfactory one, as will be explained later on, and is therefore included in square brackets.

The large difference between the result obtained in air and *in vacuo* first drew our attention to a possible influence of the size of the bowl. The experiments made to clear up this point have already been described. A few deposits were taken with the small bowl *in vacuo* and the large bowl in air; although the two effects counteract each other, the deposits *in vacuo* are larger than those in air, as is shown by Table V.

On the supposition that the effect due to the size of the bowl is the same in air as it is *in vacuo*, we may combine the results of Tables IV and V, and thus find that the deposits of silver *in vacuo* are about one part in a thousand larger than those in air. The next two experiments (Table VI) were a surprise.

Table IV.—Comparison of Deposits in Air at Atmospheric Pressure and under a Reduced Pressure of about $1\frac{1}{2}$ inches.

Number of experiment.	Date.	Strength of solution in per cent.	Approximate current in ampères.	Duration of electrolysis in minutes.	Weight of deposits.		Difference in mgrms.	Percentage difference.
					Large bowl <i>in vacuo</i> .	Small bowl in air.		
1	Jan. 9	12	0·6	31	1·2468	1·2451	1·7	0·141
3	" 14	12	0·6	30	1·2005	1·1989	1·6	0·133
17	April 27	20	0·5	60	[2·0183]	[2·0144]	[3·9]	[0·195]

Table V.—Comparison of Deposits in Air at Atmospheric Pressure and under a Reduced Pressure of about $1\frac{1}{2}$ inches.

Number of experiment.	Date.	Strength of solution in per cent.	Approximate current in ampères.	Duration of electrolysis in minutes.	Weight of deposits.		Difference in mgrms.	Percentage difference.
					Small bowl <i>in vacuo</i> .	Large bowl in air.		
5	Jan. 21	12	0·7	38	1·7255	1·7243	1·2	0·070
6	" 23	12	0·6	33	1·4361	1·4350	1·1	0·078
8	" 29	12	0·6	120	5·1036	5·1014	2·2	0·043

Table VI.—Comparison of Deposits in Air at Atmospheric Pressure and under a Reduced Pressure of about $1\frac{1}{2}$ inches, the Anode *in vacuo* being small.

Number of experiment.	Date.	Strength of solution in per cent.	Approximate current in amperes.	Duration of electrolysis in minutes.	Weight of deposits.		Difference in mgrms.	Percentage difference.
					Small bowl <i>in vacuo</i> .	Large bowl in air.		
10	Feb. 5	12	0.6	120	4.8455	4.8477	-2.2	-0.046
11	" 7	12	0.9	86	5.1829	5.1830	-0.1	-0.000

We traced the cause of the anomalous results shown in this table. The anode of the small bowl had by repeated use been gradually dissolved; the current density was consequently increased. Under these circumstances the current becomes unsteady, polarisation effects make themselves apparent, and the deposits are no longer trustworthy. The deposits taken when the current density is too great have generally a yellow colour. We are reminded of some old experiments in which by increasing the current density black deposits were obtained on the kathode, which at one time were supposed to be a hydride of silver. Poggendorff is generally stated to have proved that the black deposit is not a compound, but silver in a finely divided state. On referring to Poggendorff's paper, his experiments do not seem convincing, and he has expressed himself with more caution than those who quoted him afterwards. He states, however, that the black deposit often suddenly changes into a light one. Some observations made by Mr. Hoskins Abrahall in the Owens College Laboratory, as well as our own experiments, lead us to believe that it is the current density at the anode more than that at the kathode, which introduces the anomalous results. When the deposits are thus untrustworthy, the current, as far as we are able to judge, is always unsteady, so that no danger arises when the silver voltmeter is used for the calibration of instruments.

At this stage of the inquiry we introduced a second bell-jar and a second voltmeter of approximately the same size as the small one previously used. The balance was also changed, and the weighings were taken on a new short-beam balance. This balance was unsteady in its indications after first setting up, and a sudden change of zero while one of the basins was being weighed renders the result of Experiment 17 doubtful. The numbers obtained in this experiment are therefore included in square brackets in our tables. Table VII gives the comparison of the deposits in air and *in vacuo* taken in basins of nearly the same size. A glance at the numbers can leave no doubt as to the reality of the increase in the deposit under reduced pressure, although the amount of the increase is a little uncertain. There is only one case (Experiment 23) in which the deposits are practically identical, and in that case it was noticed that the deposit *in vacuo* was yellow—an indication that the current density was probably just a little too large. The average difference between the deposits is about one part in two or three thousand.

In the last three experiments, which gave comparatively large differences, the solutions used were kept separate between the experiments, and this leads us to think that we had previously committed an error in mixing our solutions, which, as has already been stated, must gradually have become free of air. Experiment 29 shows, however, too great a difference; some of the silver in the bowl kept in air may have been lost in the washing.

It seems remarkable that the electro-chemical equivalent of silver as deduced from the electrolysis *in vacuo* is almost identical with that obtained in Lord Rayleigh and Mrs. Sidgwick's deposits from hot solutions.

One point as yet remains to be discussed. It was reasonable to assume that the increased deposit *in vacuo* was due to the removal of the oxygen out of the solution. In order to obtain more definite information, we took some deposits in an atmosphere of oxygen. In the first experiment the two bell-jars were exhausted, and one of them filled with oxygen, which was allowed to stand for three hours over the solution before electrolysis.

The result was as follows:—

Deposit in air	(small bowl)	1·8618
„ oxygen	„	1·8618
„	(large bowl)	1·8624

There is here no difference except that due to the size of the bowl. As it seemed doubtful whether the oxygen had in the course of three hours been absorbed to its full extent by the solution, three more experiments were made and conducted as follows—

One small basin was kept in air as before; the other was kept *in vacuo*, while the large basin was filled with a solution which after boiling had a stream of oxygen passed through until it was considered that the liquid was saturated with the gas. The solution thus prepared was kept in an atmosphere of oxygen. The comparison between the deposits in air and *vacuo* have already been given (Experiments 29, 30, 31, Table VII).

The weight of the deposits in air and in oxygen was as follows:—

Small bowl in air.	Large bowl in oxygen.	Percentage difference.
1·8495	1·8488	0·04
1·8990	1·8983	0·04
1·8989	1·8981	0·04

We attribute the consistency of these results partly, at any rate, to the fact that the solutions used in the three bowls were kept separate

In looking at the figures it must be remembered that the large bowl would, if placed in air, have given a larger deposit than the small one, so that the difference between oxygen and air is really greater than would appear from the numbers. There seems little doubt, therefore, that it is the removal of oxygen which is the cause of the increased deposits *in vacuo*.

We have made a number of experiments on the polarisation of the electrodes in our silver voltameters. It does not follow that because there is as much silver dissolved as deposited, there is necessarily complete absence of what is commonly called polarisation. In the first place, the silver is dissolved from a compact sheet which is in a molecular condition different to the crystalline form in which it is deposited. Secondly, the silver is dissolved into a more concentrated solution than that out of which it is deposited, and, as Warburg has pointed out, it is very difficult to distinguish polarisation effects from electromotive forces due to differences of concentration. Our experiments have shown a small but very consistent polarisation of 0.007 volt, which was the same *in vacuo* and in air.

If, after the polarising current has passed, the anode is taken out, and replaced after the liquid has been thoroughly stirred, the polarisation is reduced, but still exists to the extent of about one-third the original value. The electromotive force of polarisation does not seem to be different when the platinum basin is partially or completely covered with silver; but the greater the amount of silver the more slowly does the polarisation die out. We cannot draw any very definite conclusions from these observations, but it seemed worth while to put them on record.

We do not wish to enter into a full discussion of the explanation of our results, but only draw attention to two phenomena investigated by Helmholtz and Warburg respectively. It was shown by Helmholtz that the small current which passes through water under the action of electromotive forces insufficient to decompose it is due to the presence of dissolved oxygen. If part of the current in a solution of silver nitrate is conveyed by hydrogen atoms, no hydrogen could separate out as gas, but a recombination with the dissolved oxygen could take place. A small fraction of the current might be conveyed precisely in the way described by Helmholtz. In a subsequent paper,* Helmholtz draws from thermodynamic principles the conclusion that "in very dilute solutions or in acids containing no salts at all, metals, which we otherwise consider unoxidisable in the acid, may dissolve to a small extent with evolution of hydrogen."

Warburg,† in an important paper, shows that voltaic cells may be formed by two pieces of the same metal, dipped into the same solu-

* 'Collected Works,' vol. 2, p. 978.

† 'Wiedemann, Annalen,' vol. 38, p. 321.

tion, if the solution surrounding one of the electrodes contains oxygen in solution. He establishes, further, the fact that in such cases the metal actually enters into solution, and explains thereby a variety of phenomena. From his observations there seems little doubt that even in a solution of silver nitrate silver may dissolve to a slight extent. The amount so dissolved is possibly increased when the silver is in the nascent state, and may then become measurable.*

We draw the general conclusion from our experiments that the true electrochemical equivalent of silver is probably not quite one part in a thousand greater than the value given by Lord Rayleigh, but that, if the experiments are conducted in air and under circumstances similar to those under which Lord Rayleigh's measurements were made, the anomalies described by us do not interfere with the use of the silver voltameter as a current measurer. On the contrary, the fact that we were able to show the existence of systematic differences amounting to not more than two parts in ten thousand is a proof of its trustworthiness.

VI. "A new Mode of Respiration in the Myriapoda." By F. G. SINCLAIR (formerly F. G. HEATHCOTE), M.A., Fellow of the Cambridge Philosophical Society. Communicated by A. SEDGWICK, F.R.S. Received January 8, 1892.

[This is a new version of the Paper read November 26, 1891. See *ante*, p. 200.]

VII. "The 'Ginger-beer Plant,' and the Organisms composing it: a Contribution to the Study of Fermentation-yeasts and Bacteria." By H. MARSHALL WARD, M.A., F.R.S., F.L.S., Professor of Botany at the Forestry School, Royal Indian Engineering College, Coopers Hill. Received January 14, 1892.

[The Paper printed at page 261, *ante*, contains the substance of this Paper in abstract.]

* I have assured myself by experiment that the well-known diminution in weight of copper in copper sulphate does not take place *in vacuo*, care being taken to remove the dissolved oxygen completely. Experiments are at present in progress to investigate the electrolysis of copper *in vacuo*.—A. S.

FIG. 1.

